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Polymer Esters

Uwe Wallfahrer
Akzo Nobel Central Research
Düren, Germany

Lynnette Bowen
Akzo Nobel Chemicals Ltd.
Tunbridge Wells, England

I. INTRODUCTION

Polymer esters are a relatively new class of synthetic lubricating oil base fluids. From a chemical point of view they are positioned between typical "monomelic" esters (diesters, polyol esters) and synthetic hydrocarbons such as poly α-olefins (PAOs).

Polymer esters are copolymers of α-olefins and unsaturated diesters. Copolymers of α-olefins and unsaturated monoesters (acrylic acid esters) are commercially available, but these fluids are not referred to as polymer esters because the chemical and performance properties are quite different.

The roots of the polymer esters lie in the 1970s, when α-olefins became an ever cheaper raw material by virtue of the polymerization of ethylene, and the chemical industry started to investigate the potential of α-olefin derivatives in various markets. Originally aimed at the application of release agents for thermoplastics, the class of polymer esters soon was seen to exhibit high load-carrying capacity (unsurpassed at the time), which made them predestined for use as lubricating oil base fluids.

During the early 1980s the first commercial products appeared on the market [1]. They were originally offered as a replacement for brightstock; their high viscosity (15–65 mm^2/s at 100°C), relative to typical monomelic esters available at that time, gave two-stroke engine oils an enhanced lubricity. Subsequently polymer esters were found to give an antiwear boost in four-stroke engine oils. At that time however the relatively high price of the polymer esters versus other synthetic components, together with the oil formulators' inexperience with optimized blending of these new compounds, prohibited their use on a larger scale.

The first major breakthrough of this technology occurred in the late 1980s in the metalworking fluid market, when the use of chloroparaffins was banned in Germany. The high inherent

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lubricity of the polymer esters and their ability to form powerful synergies with antiwear additives often made these compounds the only available alternative to chloroparaffins.

With the requirements for lubricating oils in combustion engines also becoming more and more stringent, polymer esters started to penetrate this market. Today they are successfully established as synthetic component for reducing wear in automotive and industrial fluids worldwide.

II. CHEMISTRY

A. Structure of the Polymer Esters

Polymer esters are copolymers of α-olefins and maleic or fumaric acid esterified with short or medium chain length alcohols. Polymer ester types with long ester side chains (coco, tallow esters) are also commercially available, however these products are solids and typically used as wax lubricants rather than as lubricating oil base fluids.

The idealized chemical structure of a polymer ester is shown in Fig. 1. Attached to the hydrocarbon backbone are alternating hydrocarbon side chains and pairs of ester side groups. The ester pairs interact, imparting to the polymer esters special properties (e.g., high thermal and hydrolytic stability) that differentiate polymer esters from α-olefin–acrylic acid ester copolymers.

In practice α-olefins and unsaturated esters do not form a strictly alternating copolymer. By careful choice of reaction conditions and raw materials, it is possible to prepare polymer esters with an excess of olefins or esters. In this way it is possible to produce polymer esters with a broad polarity range, giving compatibility with very unpolar, high viscosity poly α-olefins (polymer esters with an excess of olefins and longer ester side chains) to completely water-soluble compounds (polymer esters with an excess of ethoxylated ester side chains).

B. Manufacturing Routes

Polymer esters are produced from α-olefins and maleic or fumaric esters [2,3]. The reaction is a radically induced polymerization process as outlined in Fig. 2. The unique properties of polymer esters are achieved by choice of the radical initiator and by adjustment of reaction conditions (e.g., polymerization temperature, dosing rate of raw materials). As with PAOs, after the polymerization step the polymer esters contain residual double bonds, which sometimes make it necessary to hydrogenate the polymer to improve the final stability of the fluid, particularly for the lower molecular weight copolymers.

A second route used to manufacture polymer esters is to begin by reacting an α-olefin with maleic anhydride and subsequently esterifying the intermediate polymeric anhydride with the

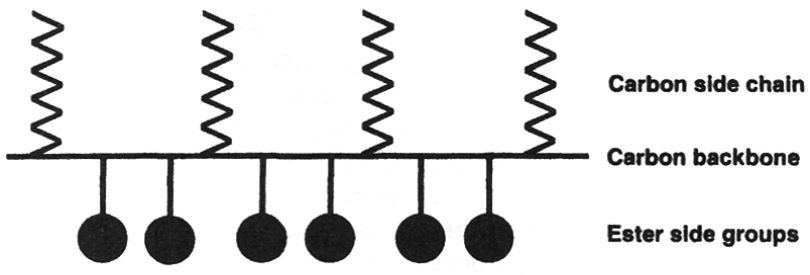

Figure 1 Idealized molecular structure of polymer esters.

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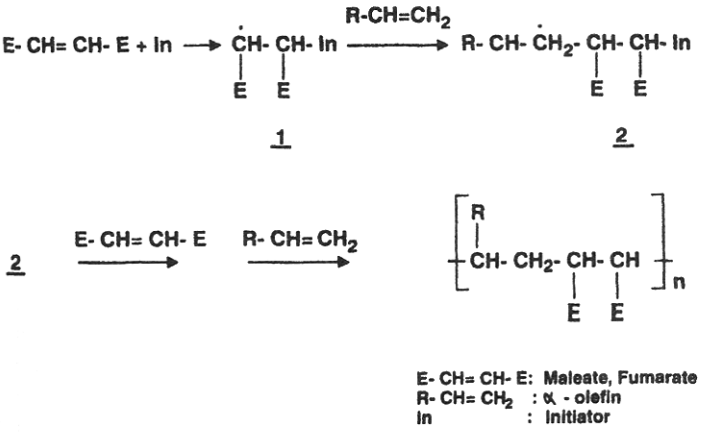

Figure 2 The chemical reaction mechanism of polymer ester formation.

desired alcohol (Fig. 3). Polymer esters produced by this method are usually higher in molecular weight or product viscosity, respectively [4].

III. PHYSICOCHEMICAL PROPERTIES OF THE POLYMER ESTERS

A. Rheology

Rheology is probably the most important property of any lubricating oil base fluid. The viscosity behavior of a lubricant, depending on oil temperature, pressure, and shear rate, is crucial for its ability to form oil films that reduce friction and wear.

1. Viscosity

Polymer esters typically are colorless viscous liquids. A wide range of viscosities currently available to the commercial lubricating oil market, ranging from 6 mm^2/s to more than 700

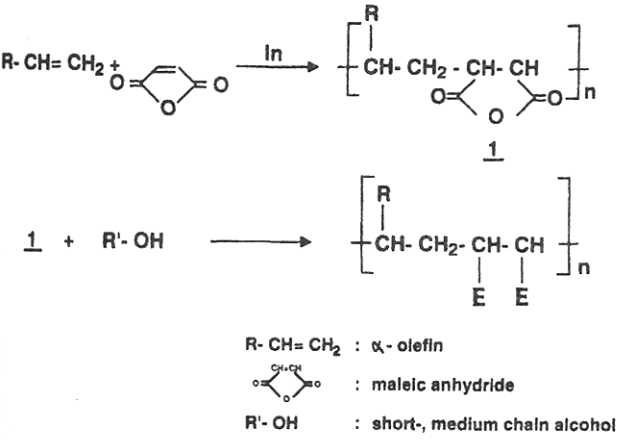

Figure 3 Alternative synthetic route to the manufacture of polymer esters.

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mm^2/s at 100°C. The average molecular weights M_n range from 700 to in excess of 7000 daltons. Figure 4 shows the relative molecular weights and kinematic viscosities of the polymer esters.

The chain lengths of the monomers used to produce polymer esters have only a limited influence on the final viscosity of the fluid, which is contrary to the case of diesters or polyol esters, where product viscosity can be significantly influenced by choice of appropriate acids and/or alcohols.

2. Elastohydrodynamic Film Thickness; Viscosity–Pressure Coefficients

Elastohydrodynamic lubrication occurs between loaded, rubbing nonconforming surfaces as found in systems such as cams and rolling element bearings. In such systems, very high pressures are produced in the rubbing contacts, and these have two important effects. First, they result in local elastic deformation of the surfaces, to produce a small, flattened contact zone, typically 0.1–1 mm^2 for steel surfaces. Second the high pressure causes the viscosity of the oil in the contact inlet to increase to many times its normal, atmospheric pressure value. These two effects couple and result in the formation of an "elastohydrodynamic" oil film (EHD film) between the surfaces. The ability of an oil to build an efficient EHD film is prerequisite to controlled wear rates and sliding contact fatigue lives [5].

The central film thickness of an oil at very high pressures is proportional to its viscosity-pressure coefficient α [6]. The higher the value of α, the more efficient the oil under high pressure. Naphthenic mineral oils exhibit a relatively high α value, whereas synthetic base fluids (e.g., PAOs or diesters) are significantly inferior in this respect. As shown in Fig. 5, the α values of polymer esters are more or less equivalent to that of mineral oil.

3. Viscosity–Temperature Behavior; Pour Point

The viscosity index (VI) of the polymer esters ranges from 140 to more than 250, correlating closely to the average molecular weight (i.e., viscosity) of the polymer ester types. Polymer esters, like other synthetic lubricating oil base fluids, show a general trend to higher viscosity indices with increasing molecular weights. The VI of both monomeric esters and polymer esters can be improved by choosing straight chain raw materials (e.g., no branched ester side groups).

Apart from the nonhydrogenated types, the pour point of polymer esters is usually higher than for typical ester base fluids of low viscosity. The pour points range from approximately −45°C for the lower viscosity polymer esters to about −15°C for the very highly viscous types. Branched raw materials improve the pour point of the base fluids, opposite to the effect on the viscosity index, where a detrimental effect is seen. The distribution of the monomers in the ester copolymer (more randomly distributed or more alternating) has an influence on the pour

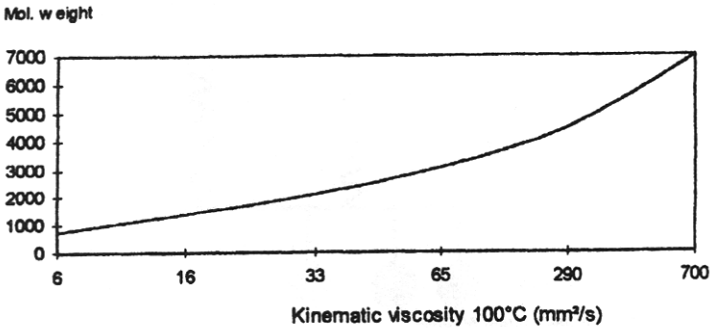

Figure 4 Average molecular weight versus kinematic viscosity for the polymer esters.

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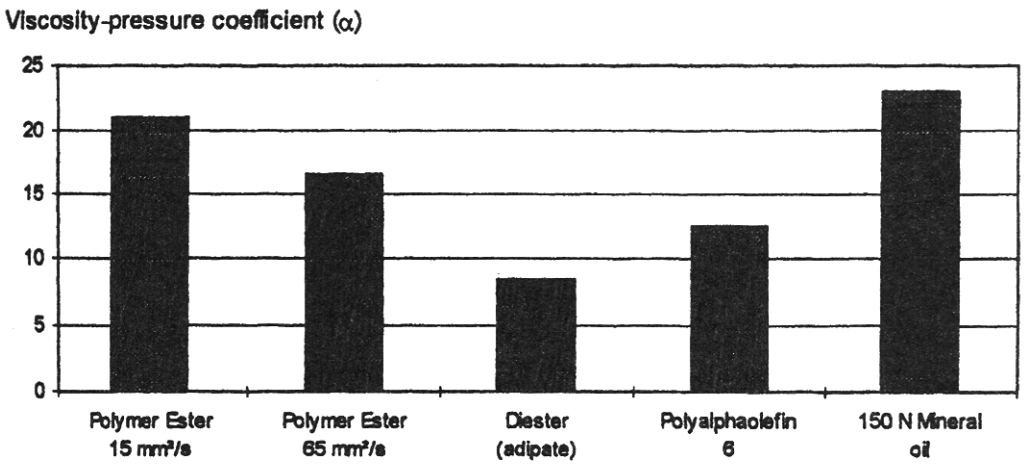

Figure 5 The viscosity–pressure coefficients of the polymer esters versus those of other fluids.

point of the fluid. In practice this calls for a very careful selection of raw materials and maintenance of reaction conditions to achieve the optimum balance between high VI and low pour point. Hydrogenation always significantly increases the pour point of the fluid.

Viscosity data and pour points of some typical polymer esters together with those of other synthetic base fluids are given in Table 1.

4. Viscosity Behavior in Blends

In blends with PAOs or mineral oils, polymer esters exhibit a unique property, namely, a surprisingly low thickening effect, as demonstrated in Fig. 6. Other base fluids of comparable viscosity result in higher viscosities in similar blends.

In formulating, this physical benefit allows the use of the higher viscosity polymer ester types (15–65 mm^2/s at 100°C) in substantial concentrations for 5W or 10W automotive engine oil formulations.

With the very high viscosity polymer ester types (300 mm^2/s and above), this low thickening effect is even more pronounced: a 40% solution of a 700 mm^2/s polymer ester in PAO 6 has

Table 1 Viscosity Data and Flow Properties of Some Polymer Esters Compared to Other Synthetic Base Fluids

Base fluid	Kinematic viscosity (mm^2/s) At 40°C	Kinematic viscosity (mm^2/s) At 100°C	Viscosity index	Pour point (°C)
Polymer ester 6, mm^2/s	27	5.6	138	−42
Polymer ester 34, mm^2/s	340	34	139	−32
Polymer ester 300, mm^2/s	4300	300	225	−18
PAO 6	33	6.0	140	−57
PAO 40	403	40	151	−40
Diisodecyladipate (DIDA)	15.1	3.6	136	<−70
Trimethylolpropane triheptanoate	15.0	3.5	124	−60
Pentaerythritol tetraisooctanoate	75.9	8.44	75	−55

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Figure 6 The low and high temperature viscosities of a 40 mm^2/s polymer ester versus those of a 40 mm^2/s poly(α-olefin) in 150 N mineral oil (20% solutions).

a lower viscosity than a solution of PAO 100 in PAO 6 despite the sevenfold viscosity of the polymer ester compared to that of PAO 100 (Fig. 7).

For this reason, in addition to the performance credits, high viscosity polymer esters have found their use in multigrade automotive gear oils as a successful replacement for high viscosity PAOs. On the other hand, this effect makes that use of very high viscosity polymer esters as VI improvers possible only selectively. Acrylate copolymers of similar viscosity are successfully used as VI improvers.

5. Viscosity Under High Shear Rates

Typical monomeric esters do not change their viscosity under high shear rates; they exhibit Newtonian behavior or are shear-stable. However, polymers used in lubricants often are non-Newtonian fluids, which means that their viscosity drops under high shear rates either temporarily (i.e., followed by a return to the original viscosity at low shear rates) or permanently (i.e., the viscosity remains low because the polymer chains have experienced physical cleavage under the shear stress). A permanent drop in viscosity is usually not desired in lubricating oils, particularly not in automotive engine oils and gear oils.

In spite of their polymeric nature, polymer esters are both temporarily and permanently shear-stable. Even a 700 mm^2/s polymer ester exhibited a shear loss of less than 1 % after 20 hours in the well-known taper roller bearing shear test (CEC L-45-T-93).

B. Lubricity of the Polymer Esters

1. Inherent Lubricity

All ester-type compounds are known to be good lubricants as a result of their molecular structure: the lone electron pairs of the oxygen atoms of the ester linkages tend to form electrostatic bonds with the metal surface. The more ester groups present at a given molecular weight, the more

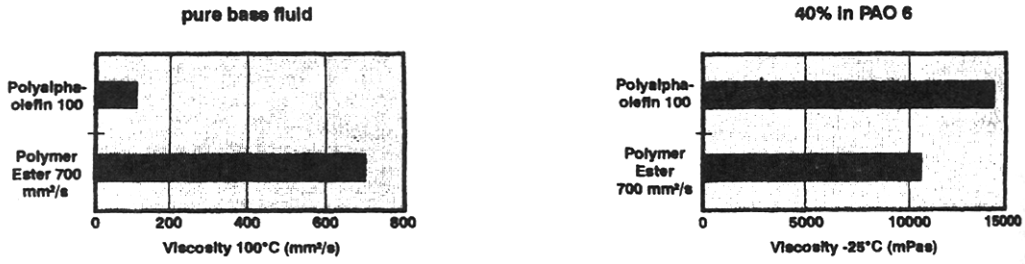

Figure 7 The low temperature viscosity of a 700 mm^2/s polymer ester versus PAO 100 in PAO 6.

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polar the ester molecule, and the higher generally the affinity of the ester to metals. Within the field of esters, the class of polymer esters exhibits the highest inherent load-carrying capacity currently known, because of two special effects:

Their polymeric nature in conjunction with the presence of many ester side groups in each polymer chain.
The ester side groups occur in pairs.

These two effects together are responsible for a very high affinity to metal surfaces, sometimes described as the "caterpillar effect."

The superior inherent lubricity of the polymer esters can be demonstrated in the Reichert Friction and Wear Tester, which offers a simple, quick means of evaluating lubricating oil base fluids. The test machine consists of a rigidly mounted test roll, which is pressed against a revolving friction wheel by means of leverage. The friction wheel is immersed with its lower third in the test fluid, so that there is always sufficient fluid at the contact surface of test roll and friction wheel (cf. Fig. 8). The crosswise arrangement of the axles of the test roll and the friction wheel results in the formation of an elliptically shaped wear scar; its size indicates the load-carrying capacity of the test fluid. To be able to compare test results, the wear scar of the test fluid is usually reported as a percentage of the wear scar to a reference fluid set to 100%. For oil-soluble candidates, the reference fluid is 150 N mineral oil.

Figure 9 compares the Reichert wear results of the polymer esters to those of other mineral and synthetic base fluids. Because product viscosity significantly influences load-carrying capacity (the higher the viscosity, the better the lubricity of a base fluid), the lubricity versus viscosity of the base fluids is given.

As with typical esters, within the class of polymer esters (apart from the product viscosity) the lubricity is also dependent on the polarity of the polymer ester types. The greater the number of ester groups incorporated in the ester copolymers, the higher their inherent lubricity.

2. Synergy with Antiwear/Extreme Pressure Additives

Although the inherent lubricity is an important feature of every lubricating oil base fluid, their synergy with antiwear/extreme pressure (AW/EP) additives is even more important. It is the AW/EP additives in a lubricating oil that are used to prevent detrimental metal–metal contacts

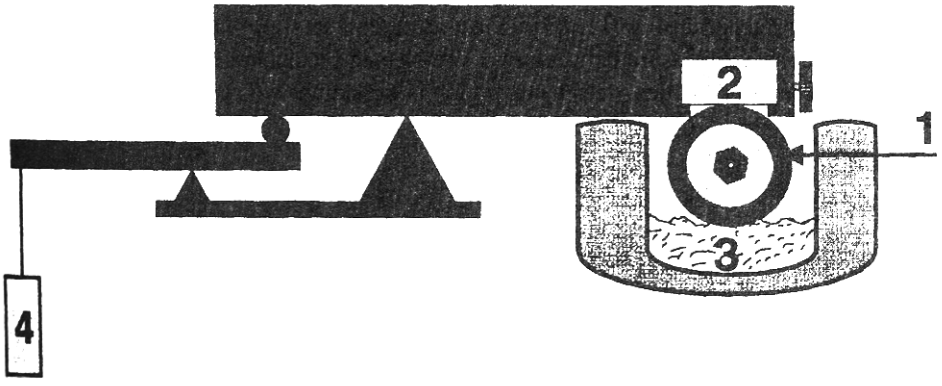

Figure 8 Operation principle of the Reichert friction and wear tester: 1, spinning steel wheel; 2, metal specimen; 3, test fluid; 4, load.

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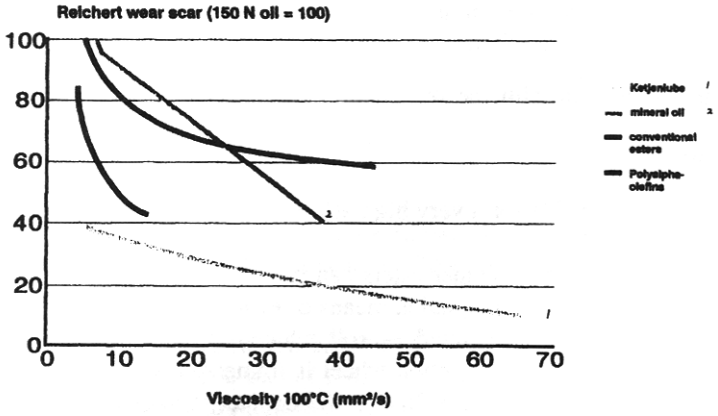


Figure 9 Reichert test results of some polymer esters compared to other base fluids.

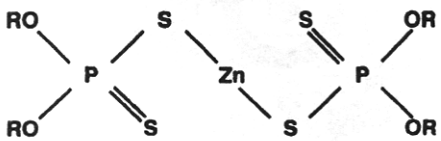
under severe conditions of high loads or low speeds of the moving parts, under "extreme pressure' ' or boundary lubricating conditions.

A typical and probably the most widely used AW/EP additive is zinc dialkyldithiophosphate (ZDDP; Fig. 10). It is known that many diesters and polyol esters act synergistically with the various ZDDP types, derived from primary, secondary, or aryl alcohols. The resulting lubricity of the combination ester/ZDDP is higher than the sum of the performances of the two components.

The reason for this beneficial behavior of esters has been found to be a complex formation of the esters with ZDDP, resulting in a decrease of the decomposition temperature of the ZDDPs [7]. It is not the ZDDP but rather its in situ created phosphorus- and sulfur-containing decomposition products that are the true wear-reducing agents, and thus the formation of these decomposition products means a wider temperature range of AW/EP activity of the ZDDP.

The efficient synergy of polymer esters with ZDDP has been explained in terms of the drastic reduction of the decomposition temperature of the ZDDP, which permits the wear protection of the ZDDP decay products to start at even lower oil temperatures.

This beneficial effect can be demonstrated in the Falex Pin & Vee Wear Test according to ASTM D-2670, as sketched in Fig. 11. In this test a rotating steel pin is immersed in the test oil and subject to constant pressure between two Vee-shaped blocks in a "nutcracker" device. The wear is expressed in so-called wear teeth, which is the number of teeth by which the gear



R = n- or iso-alkyl, aryl

Figure 10 Chemical structure of zinc dialkyldithiophosphate (ZDDP).

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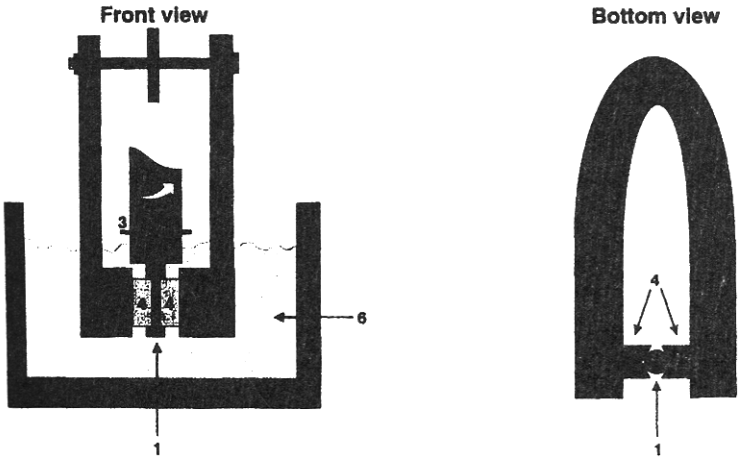

Figure 11 Two schematic views of the Falex Pin & Vee wear tester: 1, steel pin; 2, holder; 3, safety pin; 4, Vee blocks; 5, ''nutcracker'' device; 6, test fluid.

must be turned to maintain the constant pressure of the Vee-blocks on the pin during the test. If the wear becomes too severe, a safety pin breaks and stops the test.

The synergistic effect of the polymer esters with ZDDPs is efficiently demonstrated in this test. Whereas solutions of ZDDPs or polymer esters alone in mineral oil do not survive the test, the synergistic combination ZDDP/polymer ester results in a very low number of wear teeth. Diesters or polyol esters can also show this synergy, but not to the same extent (Fig. 12).

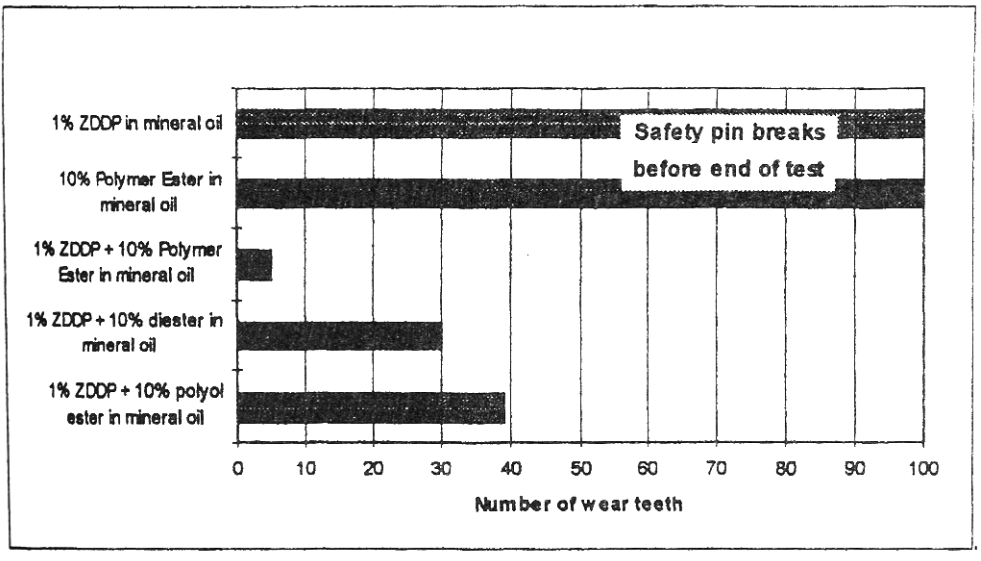

Figure 12 Synergy of a 34 mm^2/s polymer ester and other esters with a zinc dialkydithiolphosphate (short chain secondary ZDDP) demonstrated in the Falex Pin & Vee wear tester (ASTM D-2670).

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Table 2 Flash Points and NOACK volatilities (ASTMD-5800) of Some Polymer Esters Compared to other Synthetic Base Fluids

Base fluid	Flash point (°C)	NOACK volatility (%)
Polymer ester 6, mm^2/s	230	12
Polymer ester 34, mm^2/s	250	3
Polymer ester 300, mm^2/s	280	0.7
PAO 6	235	7
PAO 40	272	0.8
Diisodecyladipate (DIDA)	245	15
Trimethylolpropane triheptanoate	220	8.0
Pentaerythritol tetraisodecanoate	250	1.5

C. Stability of the Polymer Esters

1. Thermal Stability

Typical monomelic esters are known to exhibit a superior thermal stability over mineral oils. Owing to the absence of hydrogen atoms in β position to the ester linkages, the polyol esters are extraordinarily stable, which makes them suitable for use in jet engine lubricants, where the extremely high requirements of thermal stability can be met only to a limited extent by diesters, and not at all by mineral oils.

A gross indication for the thermal stability of a lubricating oil base fluid is their flash point and their (NOACK) volatility. The latter is measured by heating an oil sample at 250°C and determining the weight loss in percentage after one hour. Some typical flash points and NOACK volatilities of polymer esters compared to other synthetic base fluids are shown in Table 2.

A more precise method than the NOACK volatility test is thermogravimetric analysis (TGA), where the weight loss of the candidate is recorded versus time and temperature. The TGA curves of a typical polymer ester together with the curves of other lubricating oil base fluids are shown in Fig. 13.

Most polymer ester types exhibit a thermal stability similar to that of typical diesters or

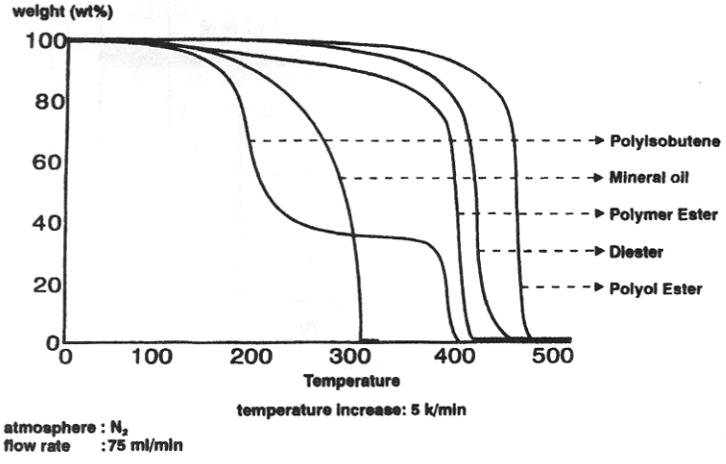

Figure 13 Thermogravimetric analysis of some lubricating oil base fluids.

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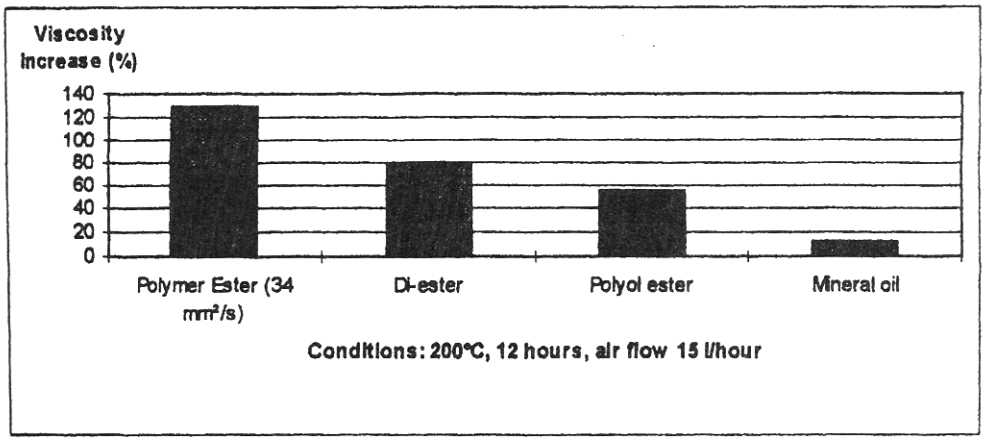

Figure 14 Thermo-oxidative stability data according to IP 48 of some lubricating oil base fluids.

PAOs; however they do not reach the superior stability of the polyol esters. For this reason polymer esters are usually not found in jet engine lubricants.

2. Oxidative Stability

One of the most important properties of an oil, especially for engine oils, oxidative stability gives a measure of the oil's aging characteristics in an oxidative environment. Oil oxidation, which results in a viscosity increase and sludge/varnish formation on the engine parts by radically induced polymerization processes, is a major limiting factor of the lifetime of an engine oil.

There are many tests available to describe the oxidation characteristics of an oil. Usually the oil is heated to a specified temperature while air is bubbled through the sample at a specified rate. After the test, acid number increase, viscosity increase, and weight loss are determined.

Without the addition of antioxidants, diesters as well as polyol esters show inferior oxidation stability to that of mineral oils, which inherently contain nitrogen- and sulfur-bearing compounds that act as natural radical scavengers. The polymer esters are inferior to diesters in this respect, as is demonstrated in thermo-oxidative stability test according to IP 48 (Fig. 14).

In practice no lubricating oil base fluid is used without the addition of an antioxidant. When blended with antioxidants, polymer esters, like diesters and polyol esters, exhibit oxidative stability superior to that of mineral oils (Fig. 15).

Residual double bonds in the polymer ester chains have a negative effect on their oxidative stability that cannot be completely compensated for by the use of antioxidants. For this reason the lower molecular weight polymer esters are hydrogenated to give the oxidative stability demanded for their use in automotive engine oils.

3. Hydrolytic Stability

Hydrolytic stability is a special feature of ester-type base fluids. It is part of the chemical nature of all esters to tend to hydrolyze, to cleave back into their acid and alcohol components, in the presence of water. This reaction is catalyzed by free acids that are formed during the reaction; the hydrolysis is an autocatalytic process. Esters should have the lowest acid number possible.

Compared to diesters and polyol esters (which usually have acid numbers below 0.1 mg

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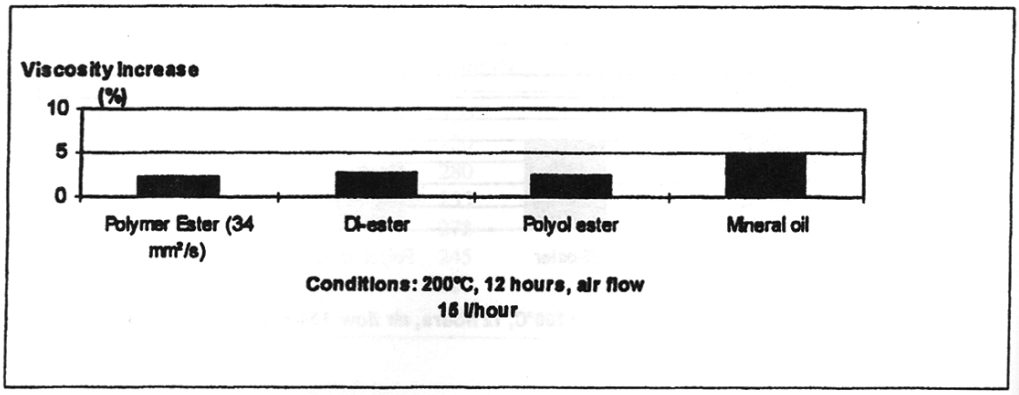

Figure 15 Thermo-oxidative stability data according to IP 48 of base oils in the presence of suitable antioxidants.

KOH/g), the polymer esters exhibit rather high acid numbers, typically around 0.3 mg KOH/g. Nevertheless they are superior to most of the "conventional" esters in terms of hydrolytic stability owing to the special molecular geometry of the polymer ester chains. In a lipophilic environment (e.g., a solution in mineral oil), the ester linkages are "buried" inside hydrocarbon coils derived from the polymer backbone and side chains; the steric hindrance thus imparted protects them from attack by water. This special geometry also stays essentially in place in aqueous emulsions (soluble oils), thus making the polymer esters feasible components of soluble cutting fluids. The hydrolytic stability of a typical polymer ester compared to other esters is shown in Fig. 16.

Hydrolytic stability improves as molecular weight increases. The resistance of polymer esters to hydrolysis is so high that it is not possible to determine a saponification number for these compounds. Even after reflux in alcoholic potassium hydroxide for several hours, no more than two-thirds of the ester bonds present in the polymer ester chains are cleaved.

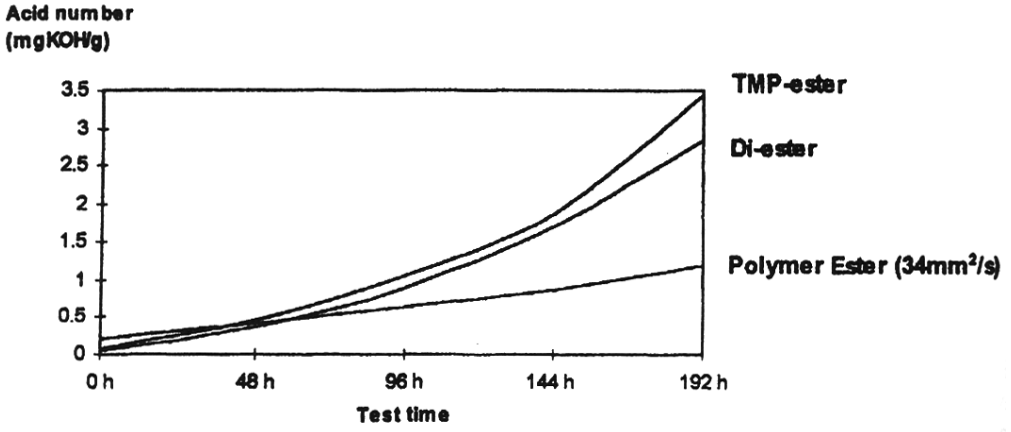

Figure 16 Comparison of a polymer ester and two other esters for hydrolytic stability (total acid number according to ASTM D-2619).

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D. Compatibility of the Polymer Esters

1. Compatibility with Other Lubricating Oil Base Fluids and Additives

As mentioned earlier, polymer esters exist in a wide range of polarities. Most polymer esters based on nonethoxylated alcohols are compatible with mineral oils and the commonly used lubricating oil additives.

With the very low polarity poly(α-olefins), especially the higher viscosity PAOs, polymer esters with a high degree of ester side groups can give compatibility problems, in particular at low temperatures. For this reason, only polymer esters of lower polarity, with a lower degree of ester side groups in the polymer chains, are used as blend components with high viscosity PAOs.

The polarity of a polymer ester is measured by an infrared (IR) method and is expressed by the ratio of the absorption intensities of the ester carbonyl bond and the hydrocarbon bond ($v_{C=o/C-H}$); that is, the higher this ratio, the more polar the polymer ester. Usually all polymer esters with a $v_{C=o/C-H}$ of less than 1.1 are compatible with PAO.

> Remark: The nonpolarity index NI [= (total number of C atoms × molecular weight)/(number of ester groups × 100)], a common formula for the calculation of the polarity of a monomeric ester [8], is not applicable to polymer esters. According to this formula, all polymer esters would be extremely low in polarity because of their very high molecular weight compared to monomeric esters.

Apart from the polarity, the molecular weight of the polymer esters as well as the distribution of hydrocarbon and ester side chains within the polymer chain influence compatibility. The lower the molecular weight, the better the compatibility of the polymer ester at a given $V_{C=0/C-H}$ with low polarity base fluids.

2. Compatibility with Elastomers

A lubricating oil base fluid should not chemically or physically attack the elastomer materials used in the manufacture of oil seals designed to prevent leakages. Mineral oil base stocks are almost ideal in their neutral behavior toward seals. Usually synthetic base fluids with a polarity lower than that of mineral oils (e.g., PAOs) tend to exert a seal-shrinking/hardening effect on elastomers that results from the extraction of soluble additives from the elastomer and fluids much higher in polarity than mineral oils. Esters, for example, tend to become absorbed in the elastomer, swelling the seals.

The effect of polymer esters on oil seals is closely related to their polarity and molecular weight. Lower molecular weight types of higher polarity have a seal-swelling effect, whereas high molecular weight polymer esters of low polarity may have even a slight seal-shrinking effect. Most polymer ester types however are more or less neutral to the seal materials in use today.

3. Compatibility with Metals and Paints

Polymer esters like diesters or polyol esters exhibit excellent compatibility to the metals typically used in the manufacture of engine parts, metalworking tools, machined parts, and so on; there are no corrosive or leaching effects. Unlike, for instance, polyalkylene glycols, they do not dissolve paints or coatings of operating machines or shop floors.

E. Health, Safety, and Environmental (HSE) Aspects

Besides such performance aspects as lubricity or stability, the HSE requirements of a lubricating oil base fluid have become increasingly more important during the recent years. Specifically,

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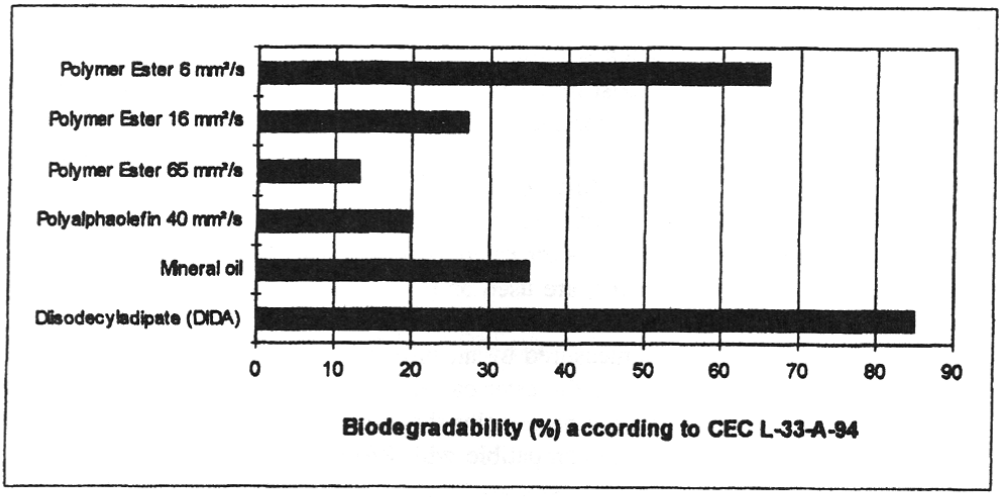

Figure 17 Biodegradability of polymer esters compared to other base fluids.

lubricating oil should not affect human health or the environment. Particular attention nowadays is paid to the effects base oils can have on aquatic media or soils. Major criteria in this respect are the biodegradability of the base fluid as well as its toxicity to fish and bacteria.

1. Biodegradability

Biodegradability of a lubricating oil base fluid usually is understood in terms of degradation by bacteria in an aqueous environment, because virtually all the common biodegradability tests are carried out in aqueous media. The most widely used test for lubricating oils today probably is the CEC L-33-A-94 test, which originally was meant to determine the biodegradability in lakes of two-stroke outboard engine oils. The test principle is based on measuring the disappearance of organic carbon by monitoring the infrared absorption of the carbon–hydrogen bonds after 21 days. Most monomeric esters show good to excellent biodegradability in this test. Natural esters like vegetable oils are more or less completely degraded within a few days.

Lack of biodegradability is one of the weak points of the majority of compounds in the polymer ester range. Apart from the very low viscosity types, they usually exhibit an inherent but limited biodegradability comparable to that of PAOs or mineral oils. As one would expect, the biodegradability rapidly decreases with increasing viscosity or molecular weight, respectively (Fig. 17). However, in combination with other base fluids a surprisingly high biodegradability of the whole system sometimes is found [9].

2. Toxicology

The polymer esters, like most diesters and polyol esters, are regarded as harmless to man and the environment. They have very high LD_{50} figures, do not irritate skin or eyes, and show no mutagenic activity. According to tests with selected polymer ester types, they are not skin sensitizing.

Their toxicity to fish, daphnia, and bacteria is low. Based on these test results, the whole class of polymer esters received a ranking of 1 in the German water-endangering class system (WGK); their lack of biodegradability prohibited a ranking of 0 (not water endangering).

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IV. APPLICATION AREAS

Polymer esters are mainly used in areas calling for high lubricity and stability, where cost-performance benefits can be demonstrated. Included are all automotive lubricants, as well as gear oils and heavy-duty metalworking fluids. In less demanding areas (e.g., hydraulic fluids, compressor oils), polymer esters usually are not used.

A. Four-Stroke Engine Oils

Synthetic oils for gasoline or diesel engines are usually based on PAO/ester blends. They offer a variety of advantages over mineral oil based lubricants, probably one of the most important being improved low temperature flow properties. In addition, the use of esters normally imparts better wear protection. Because of their powerful synergy with antiwear/EP agents, the polymer esters allow for especially efficient wear reduction, which in practice results, for instance, in very low cam nose wear.

Based on their special comblike structure with unpolar as well as polar side groups, the polymer esters also assist in keeping engines clean, an effect that is appreciated in particular in diesel engine oils.

Use of the higher molecular weight polymer esters in 0W oils is restricted because of their rather high product viscosities.

B. Two-Stroke Engine Oils

Their inherently high load-carrying capacity leads to the frequent use of polymer esters in semisynthetic and synthetic two-stroke oils to improve the antiwear properties of the oils. A secondary benefit is their especially clean burning, without giving rise to smoke or hazardous fumes.

On the other hand, the lack of biodegradability of the polymer esters restricts their use in two-stroke oils mainly to motorbike oils. They are not used in chain-saw oils or outboard engine oils in Germany or the Scandinavian countries, where oils must be readily biodegradable.

C. Gear Oils

In recent years the higher viscosity polymer ester types have been increasingly used as base fluids for multigrade automotive gear oils. Apart from better inherent lubricity, their main advantages over the normally used high viscosity PAOs are an equal or even better low temperature viscosity combined with better compatibility with lubricating oil additives [10].

D. Metalworking Fluids

The quality of metalworking fluids has improved dramatically over the past years, which has resulted in longer lifetimes of both neat oils and soluble oils (emulsions). Among the factors driving the search for better performing fluids have been more demanding operating conditions, the needs to ensure extended tool life and to accommodate higher cutting/forming speeds, and heavier requirements on the machined parts (e.g., narrower tolerance, better surface finish).

Polymer esters are widely used in high performance, heavy-duty metalworking fluids. In this area their biostability is an advantage. In soluble oils, this property of the polymer esters together with their resistance to hydrolysis, which prevents salt formation, assists in achieving increased life in use with emulsions. The synergy of the polymer esters with antiwear/EP additives results in very low tool wear and, therefore, longer tool life.

Sometimes the high affinity to metals of the polymer esters is a drawback in metalworking.

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Table 3 Relative Prices of Lubricating Oil Base Fluids

Fluid	Mineral oil	Polyisobutenes	Polyalkyle-glycols	Poly (α-olefins)	Diesters	Polyol esters	Polymer esters
Relative price	1	2–3	2–4	2–6	2–4	3–6	6–10

For example, it can be difficult to remove polymer esters from machined parts during postprocessing cleanup. However with correct technology removal is possible.

At present, a special issue in the metalworking industry in Europe is the use of chloroparaffins (chlorinated hydrocarbons), which are crucial to successful heavy-duty processing in, for example, the cutting of stainless steel. Short chain chloroparaffins, which are the most widely used types in metalworking fluids, will be banned in most European countries from 1999 on and are already banned in Germany. The use of polymer esters together with antiwear/EP agents in various instances is the only alternative that will permit the achievement of the same performance afforded by the use of chloroparaffins.

V. MANUFACTURE, MARKETING, AND ECONOMICS

1. Manufacturers of Polymer Esters

The only supplier of the polymer esters is Akzo Nobel BV, a multinational chemical company with headquarters in the Netherlands. Since the technology for making polymer esters is covered by patents [3,4], no other suppliers are expected to emerge on the market in the foreseeable future.

2. Cost-Effectiveness of Polymer Esters

Polymer esters are at the top end of the market compared to other synthetic lubricating oil base fluids (Table 3). However, their outstanding properties justify their use, especially in demanding areas like heavy-duty metalworking fluids, which pose operating problems that can hardly be solved without using polymer esters.

VI. THE FUTURE OF POLYMER ESTERS

The market for polymer esters has constantly increased during the last decade. With the performance requirements especially for automotive engine oils becoming more and more stringent, the justification for the use of expensive synthetic polymer esters is likely to increase further.

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Appendix Examples of Commercially Available Types of Polymer Esters

Physical and chemical characteristics	Method	Polymer ester type												
		Medium/high polar products				Low polar products					Unsaturated product	Water-soluble/-emulsifiable products		
Viscosity at 100°C mm^2/s	ASTM D-445	15	34	65	260	16	30	51	300	700	5.5	45	500	192
Viscosity at 40°C, mm^2/s	ASTM D 445	112	340	770	4100	120	280	540	4300	11000	27	450	12000	2500
Viscosity index	ASTM D-2270	135	139	152	200	140	138	155	225	255	138	—	—	—
Pour point °C	ASTM D-97	−28	−32	−23	−15	−31	−33	−29	−18	−10	−42	−12	+2	−4
Flash point °C	ASTM D-92	250	250	255	260	250	250	250	270	270	230	220	80	180
Total acid number, mg KOH/g	ASTM D-974	0.4	0.2	0.3	<0.1	0.3	0.3	0.2	<0.1	<0.1	1.1	ca 10	ca 65	ca 65
Density at 20°C g/cm^3	ASTM D-1217	0.93	0.96	0.98	0.99	0.92	0.94	0.95	0.96	0.96	0.93	1.06	1.02	1.05
Color (Gardner)	ASTM D-1500	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	6	2	2
Applicational properties														
Volatility NOACK, %	DIN 51581	4	3	3	1	4	3	3	1	<1	14	—	—	—
Hydrolytic stability														
Total acid number after 48 h, mg KOH/g	ASTM D-2619													
Oil phase		0.32	0.29	0.25	0.10	0.22	0.36	0.29	0.42	0.07	1.21	—	—	—
Water phase		0.18	0.24	0.03	0.24	0.14	0.27	0.08	0.11	0.02	0.13	—	—	—
Thermo-oxidative stability (200°C; 12 h; 15 L air/hr)	IP 48													
Weight loss (%)		7	6	4	4	6	6	5	4	4	15	—	—	—
Viscosity increase (%)		160	150	140	90	155	150	145	40	40	320	—	—	—
Lubricity % wear volume, (150 N oil = 100%)	Reichert													
Pure polymer ester		33	25	13	6	32	26	18	5	5	44		5% in water:	
10% Polymer ester in 150 N oil		82	70	66	50	78	74	69	60	55	80	21	—	20
Compatibility														
10% in PAO 6 (48 h at −25°C)		+	±	−	−	+	+	+	+	+	+	−	−	−
10% in 150 N oil (48 h at −10°C)		+	+	+	±	+	+	+	+	+	+	−	−	−
10% in water (48 h at 20°C)		−	−	−	−	−	−	−	−	−	−	±	±	+
Seal compatibility	CEC-L-39-X-95	Neutral behavior							Neutral behavior		Slightly swelling			
Major applicational areas		Two-stroke; four-stroke (gasoline and diesel); gear oils, hydraulic oils, greases, MWF							Gear oils (automotive; industrial)		Two-stroke; MWF	MWF (soluble oils)		

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